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The following data are taken from files submitted by the applicant.

Heat-insulating coating

The invention concerns a heat-insulating coating, which comprises one or more cholesteric, IR-reflecting layers as well as a process for its production and its application.

- 1 -

Description

The invention concerns a heat-insulating coating which comprises one or more cholesteric, IR-reflecting layers.

The problem of shielding from heat radiation is especially at hand in the insulation of residential, office, or industrial buildings. Buildings with liberally sized window areas heat up rapidly, especially in the summer, and particularly in southern regions, to a level that they have to be cooled by air condition systems with considerable energetic expense.

Common methods for heat insulation, especially for shielding against heat radiation in the wavelength range from 800 nm and 2000 nm are based on the absorption of radiation by appropriated colorants or pigments. However, the energy absorbed is given off by conduction at the most part to the insulated object or room.

It is also known to use materials which mostly reflect radiated heat.

For this purpose specialty colorants or pigments, but also graphite or gold, are often used as broad band absorbers or reflectors.

For example, naphthalo-cyanine absorbing in broad band in the infrared region (IR) or also resinous polymethine colorants are utilized as colorants. However, the IR-absorbing colorants exhibit as a serious disadvantage also a clear absorption in the visible wavelength region, so that a considerably reduction in transparency is encountered. The absorbed radiation energy is transformed into thermal energy, which is dissipated by heat conduction.

Graphite, gold, silver, or indium-tin-oxide (ITO), which are also utilized as absorbers or reflectors for IR radiation, display similar disadvantages. In this case a very low transparency is also given, especially in the visible region of the spectrum. A sufficiently uniform high transmission is ensured in the visible wavelength region only by very precise and therefore costly production of extremely thin layers. These kind of metal layers are usually applied by vapor deposition methods such as chemical vapor deposition or physical vapor deposition, which are very expensive.

It is also known as well that cholesteric, liquid-crystalline substances can reflect light in the IR region of the electromagnetic spectrum. Cholesteric (chiral nematic) liquid-crystals have been known for a long time. The first example of this kind of material was found by the Austrian botanist F. Reinitzer (Monatshefte Chemie, 9 (1888), 421). The conditions for the occurrence of the cholesteric phase is the chirality. The chiral part of the molecule can be present both in the liquid-crystalline molecule itself, as well as in a doped material added to the nematic phase, whereby the chiral nematic phase is induced. The chiral nematic phase

has special optical properties: A high optical rotation as well as a distinct circular dichroism, which is created by selective reflection of circular-polarized light within the nematic layer. As a result a maximum of 50% of the incident light of the reflection wavelength is reflected. The rest passes through the medium without interaction. The sense of rotation of the reflected light is in this case determined by the rotational orientation of the helix: A right-oriented helix reflects right circular-polarized light, a left oriented helix left circular-polarized light. The stepping height and thereby the wavelength range of selectively reflected light of a chiral nematic layer can be varied by changing the concentration of the chiral doping material. In this case a direct relationship exists between the reciprocal observed stepping height "p" and the concentration of the chiral component (x_{ch}):

$$1/p = HTP \cdot c_{ch}$$

HTP stands for Helical Twisting Power and represents the ability of the chiral doping material for twisting.

Cholesteric liquid-crystal components on the basis of cholesterol derivatives as well as photopolymeric cholesteric coatings, which contain them in the polymer, are known from US-A-4,637,896. The described cholesteric films display mostly reflection maxima in the visible wavelength region. Still, two examples for colorless films are also presented with reflection maxima at 950 to 1260 nm. These films are not suitable for heat insulation coatings because of the narrow reflection width.

Solid cholesteric films on a cellulose basis are known from US-A-5,629,055. The films are obtained from a colloid-suspension of cellulose crystallites, whereby the colloid suspension has been produced by acidic hydrolysis of crystalline cellulose. The rigid films have cholesteric properties and their reflection wavelength are supposed to be adjustable over the whole spectral range of infrared to ultraviolet radiation. The described materials are especially proposed for optical authentication materials, since printing and copying techniques can not reproduce the cholesteric effect.

US-A-5,352,312 describes a process for insulating rocket engines against heat and corrosive materials. The process comprises the use of an ablative insulation material, which contains a thermoplastic, liquid-crystalline polymer. The liquid-crystal material is, however, not cholesteric, and the insulating effect is based on the ablative effect and not on the reflection of radiant heat.

An infrared filter is known from US-A-5,016,985, which comprises a broad-band infrared filter element as well as a cholesteric liquid-crystalline filter element. The importance of the cholesteric filter element is especially based on its ability to block infrared wavelength in a precise, narrow band. The infrared filter can be used, for example, in night vision devices.

Therefore, the task of the invention is to provide heat insulation materials, which can easily be produced, which are almost completely transparent in the visible region of the electromagnetic spectrum, and which feature only a very small absorption in the near infrared as well as in the visible wavelength region of the electromagnetic spectrum.

It was surprisingly found that coatings, which contain at least one cholesteric IR-reflecting layer meet these requirements.

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The subject of the present invention is therefore a heat-insulating coating, comprising one or several cholesteric layers, which reflect in the infrared wavelength region, preferably above 750 nm, especially in the wavelength region of 751 to about 2000 nm at amounts of at least 40%, especially at least 45% of the incident radiation.

The heat insulation coating of this invention features a number of surprising advantages:

- a) Incident radiation is almost completely transmitted in the visible wavelength region, so that the coating appears transparent.
- b) Incident light in the infrared region of the electromagnetic spectrum is mostly reflected and not absorbed, so that the object to be insulated is not heated up by heat conduction.
- c) Incident heat radiation is reflected in broad band, which allows for efficient insulation of the objects.
- d) The thickness and uniformity of the coating can be varied within a wide range without significant influence on their insulation properties, so that their production is considerably less costly than that, for example, of metal-containing reflection layers.
- e) The use of ecologically and toxicologically troublesome metals is avoided.
- f) The starting materials for the production of the coating are commercially easily available; their use is therefore typically less expensive in reflection coatings than that of gold or silver, for example.

The heat insulation coating of this invention preferably features in the wavelength region of the visible light, hence, in the region of about 390 nm to 750 nm, a transmission of at least 80%, especially at least 90% of the incident radiation.

Especially preferred is a heat insulation coating of this invention, which comprises several, preferably about 2 to 20, especially about 2 to 10 cholesteric, IR-reflecting layers. It is especially preferred when the layers feature different reflection maxima in the wavelength range > 750 nm. Most preferred is when the heat insulation layer of this invention comprises several cholesteric layers, preferably a number of cholesteric layers, which can be divided by two, for example 2, 4, 6, 8, or 10, whereby the stepping height of the helical

superstructure of 2 particular, preferably neighboring, layers is the same, but their chirality different. At the same time most preferred is a heat-insulating coating of this invention, which features between layers a medium with helical superstructure of the same stepping height and the same chirality, which turns the sense of rotation of the transmitted circular-polarized light, especially a so-called $\lambda/2$ film or plate.

The use of layers of different chirality, or of a medium changing the sense of rotation of the transmitted circular-polarized light between the layers of the same chirality, can considerably increase the reflection of the heat-insulating coating of this invention. Degrees of reflection of at least 75%, especially of at least 85% relative to the incident radiation are achieved, preferably in the wavelength region above 750 nm, especially in the wavelength region from 751 nm to about 2000 nm.

The heat insulation coating of this invention is only limited with regard to its composition by it having to contain components which render by them alone or by their interaction cholesteric IR-reflecting properties to it. In principle, almost all known cholesteric monomers or monomer mixtures or polymers or polymer mixtures can be adjusted in the stepping height of their helical super structure by varying the chiral component, so that their reflection maxima are located in the IR region.

A preferred heat-insulating coating of this invention can contain in hardened condition cholesteric components or mixtures of components which have been selected from

- a) at least one cholesteric polymerizable monomer;
- b) at least one achiral, nematic polymerizable monomer and a chiral component;
- c) at least one cholesteric, crosslinkable polymer
- d) at least one cholesteric polymer in a diluent or a mixture of diluent which can be polymerized;
- e) at least one cholesteric polymer, whose cholesteric phase can be frozen by rapid cooling below the glass transition temperature; or
- f) at least one achiral, liquid-crystalline crosslinkable polymer and a chiral component.

The term crosslinking within the scope of the present invention is understood as covalent bonds of polymer components, and polymerization as the covalent bonding of monomeric components to polymers. The term hardening is understood as the crosslinking, the polymerization, or the freezing of the cholesteric phase.

An uniform orientation of the cholesteric molecule in the cholesteric layers is set by curing.

Preferred monomers of group a) are described in DE-A-196 02 848 as well as in DE-A-4 342 280, which are hereby incorporated in their entirety. Monomers of group a) comprise in particular at least a chiral, liquid-crystalline, polymerizable monomer of Formula I:



in which the variables have the following meaning:

Z^1 a polymerizable group or a rest, which carries a polymerizable group

Y^1, Y^2, Y^3 chemical components which are independent of each other, oxygen, sulfur

- 3 -

CO-O-, O-CO-, -O-CO-O-, -CO-S-, S-CO-CO-N(R)-, -N(R)-CO-, CH₂O, or OCH₂

A^1 a spacer

M^1 a mesogenic group

X a n-functional chiral rest,

R hydrogen or C₁-C₄-alkyl,

n 1 to 6

whereby the rest $Z^1, Y^1, Y^2, Y^3, A^1, M^1$ can be the same or be different if n is larger than 1.

Preferred rests Z^1 are:

CH₂=CH-, CH≡C-, *see original*

Chemical formulas - see original - Line 10

-N=C=O, -N=C=S, -O-C≡N,

-COOH, -OH, or -NH₂,

whereby the rests R can be the same or be different, and stands for hydrogen, or C₁-C₄-alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec.-butyl, or tert.-butyl. Among the reactive, polymerizable groups the cyanides can be trimerized spontaneously to cyan-urates, and are therefore preferred. The other listed groups require additional components with complementary reactive groups for polymerization. For example, isocyanates can polymerize with alcohols to urethane and with amines to ureic acid derivatives. The analogous applies to thiiranes and aziridine. Carboxyl groups can condense to polyester and polyamides. The maleic-imido group is especially suitable for radical copolymerization with olefinic components such as styrene. The complementary reactive groups can be either present in a second component of this invention, which is mixed with the first one, or they can be incorporated into the polymer network by supporting components, which contain two or more of these complementary groups.

Especially preferred groupings of $Z^1 - Y^1$ are acrylates and methacrylates.

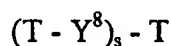
$Y^1 - Y^3$ can have the above meaning, whereby the term chemical bond is intended to mean a single, covalent bond.

All known groups are considered as spacer A^1 for these purposes. The spacers contain in general 2 to 30, preferably 2 to 12 C-atoms, and consist of linear, aliphatic groups. They can be interrupted in their chain by O, S, NH, or NCH_3 , for example, whereby these groups shall not be in a neighboring position to each other. Considered as substituents for the spacer chain are fluorine, chlorine, bromine, cyan, methyl, or ethyl. Representative spares are, for example:

Chemical formulas - see original - Line 55

whereby
m stands for 1 to 3, and
p for 1 to 12.

The mesogenic group M^1 preferably has the structure



whereby Y^8 is a bridge component according to one of the definitions of Y^1 , "s" a number from 1 to 3, and "T" the same or different bifunctional, isocycloaliphatic, heterocycloaliphatic, isoaromatic, or heteroaromatic rests.

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If "s" stands for a number >1 , the bridge components Y^8 can be the same or different.

The rest "T" can also be a ring system substituted by C_1 - C_4 -alkyl, C_1 - C_4 -alcoxy, fluorine, chlorine, bromine, cyan, hydroxy, or nitro. Preferred rests "T" are:

Chemical formulas - see original - Line 5

Especially preferred are the following mesogenic groups M^1 :

Chemical formulas - see original - Line 50

- 5 -

Chemical formulas - see original - Line 1

- 6 -

Chemical formulas - see original - Line 1

Among the chiral rests X of the components of Formula I, especially those are preferred due to their availability, which are derived from sugars, bi-naphthalene or bi-phenyl derivatives, as well as optically active glycols, di-alcohols, or amino acids. Especially the pentose and hexose and the derived derivatives from them are to be pointed out among the sugars.

Examples for the Rest X are following structures, whereby a terminal dash indicates the particular free valences

Chemical formulas - see original - Line 35

- 7 -

Chemical formulas - see original - Line 1

- 8 -

Chemical formulas - see original - Line 1

Especially preferred are:

Chemical formulas - see original - Line 45

Furthermore, chiral groups are also suitable, which exhibit following structure:

- 9 -

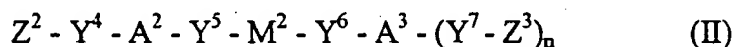
Chemical formulas - see original - Line 1

Additional examples are listed in the German application P 43 42 280.2.

"n" is preferably 2.

Preferred monomers of group a) are furthermore chiral polymerizable cholesteric derivatives as are described in DE-A-35 35 547 and in US-A-4,637,896, which are referenced here in their entirety.

Preferred monomers of group b) are described, for example, in the dissertation of H. Jonsson, Department of Polymer Technology, Royal Institute of Technology, S-10044 Stockholm, Sweden, from 1/25/1991, in DE-A-4 408 171, in DE-A-4 408 170, as well as in DE-A-4 405 316, which are referenced here in their entirety. The cholesteric mixture preferably contains at least one achiral liquid-crystalline, polymerizable monomer of Formula II



in which the variables have the following meaning:

Z^2, Z^3 have the same or a different polymerizable group, or a rest, which contains a polymerizable group,

"n" is 0 or 1

Y^4, Y^5, Y^6, Y^7 are chemical components independent of each other, oxygen, sulfur CO-O-, O-CO-, -O-CO-O-, -CO-S-, S-CO-CO-N(R)-, -N(R)-CO-, CH_2O , or OCH_2

A^2, A^3 are the same or a different spacer, and

M^2 a mesogenic group

In this case the same preferences apply to the polymerizable groups, the bridge components Y^4 to Y^7 , the spacers, and the mesogenic groups as to the corresponding variables in Formula I.

Furthermore, the mixture of group b) contains a chiral component. The chiral component causes a twisting of the achiral, liquid-crystalline phase to a chiral phase. In this case the extend of twisting depends on the ability of the chiral doping material and its concentration. Thus, the stepping height of the helix and again the reflection wavelength depends on the concentration of the chiral doping material. Therefore, a generally applicable concentration range cannot be given for the doping material. The doping material is added at an amount at which the desired reflection is obtained.

Preferred chiral components are those of Formula Ia,



in which the variables Z^1 , Y^1 , Y^2 , Y^3 , A^1 , X and "n" have the above stated meaning, and M^a is a bifunctional rest which contains at least a hetero- or isocyclic ring system.

The molecule M^a is in this case similar to the described mesogenic groups, since this way a particularly excellent compatibility is achieved with the liquid-crystalline component. However, M^a does not have to be mesogenic, since Component Ia should just cause the appropriate twisting of the liquid-crystalline phase due to its chiral structure. Preferred ring systems, which contain M^a , are the above mentioned structures T; preferred structures M^a are those of the above listed formula $(T - Y^8)_s - T$.

Additional monomers and chiral components of group b) are described in WO 97/00600 and DE-A-195 32 408, which is the basis of the former, and which are hereby included as reference in their entirety.

Preferred polymer groups of group c) are cholesteric cellulose derivatives as are described in DE-A-197 13 638, especially mixed cholesteric esters of

(VI) hydroxy-alkyl-ethers of cellulose

(VII) saturated, aliphatic, or aromatic carbonic acids, and

(VIII) unsaturated mono- and di-carbonic acids

Especially preferred are mixed esters in which the hydroxyl-alkyl rest of component VI, bonded by the ether functionality, comprises a straight chain or branched C_2 - C_{10} -hydroxy-alkyl rest, especially hydroxypropyl, and/or hydroxyethyl rest. Component VI of the used mixed esters preferably possess a molecular weight of about 500 to about 1 million. The anhydro-glucose units of the cellulose are preferably etherized with hydroxy-alkyl rests with an average molecular degree of substitution of 2 to 4. The hydroxy-alkyl groups in the cellulose can be the same kind or different. Up to 50% of them can also be replaced by alkyl groups (especially C_1 - C_{10} -alkyl groups). An example of it is hydroxy-propyl-methyl cellulose.

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Straight chain, aliphatic C_1 - C_{10} -carbonic acids, especially C_2 - C_6 -carbonic acid, branched aliphatic C_4 - C_6 -carbonic acid, especially C_4 - C_6 -carbonic acid or straight chain or branched halogen-carbonic acids are useful as mixed esters used as component VII.

Component VII can also be a benzoic acid or an aromatic-substituted, aliphatic carbonic-acid, especially phenyl-acetic acid. Component VII is especially preferred when chosen

from acetic acid, propionic acid, n-butyric acid, iso-butyric acid, or n-valeric acid, most preferred from propionic acid, 3-Cl-propionic acid, n-butyric acid, or iso-butyric acid.

Component VIII is preferably chosen from the unsaturated C_2 - C_{12} -mono or di-carbonic acids, or half-ester of this kind of carbonic acid, especially α,β -ethylenically unsaturated C_3 - C_6 -mono or di-carbonic acid or half-esters of these carbonic acids.

Component VIII of the used mixed esters is most preferably chosen from acrylic acid, methacrylic acid, crotonic acid, vinyl-acetic acid, maleic acid, furamic acid, or undecanic acid, especially from the acrylic acids or methacrylic acids.

Preferably component VI has been esterified at an average molar degree of substitution of 1.5 to 3, especially 1.6 to 2.7, most preferably from 2.3 to 2.6 with component VII and VIII. Preferably about 1 to 30%, especially 1 to 20%, or 1 to 10%, most preferably about 5 to 7% of the OH-groups of component VI have been esterified with component VIII.

The ratio of amounts of component VII to component VIII determines the reflection wavelength of the polymer.

Well suitable polymers of group c) are furthermore those described in DE-A-197 17 371, propargyl-terminated cholesteric polyester or polycarbonates.

Preferred among those components are polyester or polycarbonates with at least one propargyl-terminal group of the formula $R^3C\equiv C-CH_2-$, whereby R^3 stands for H, C_1 - C_4 -alkyl, aryl, or $Ar-C_1$ - C_4 -alkyl; (for example benzyl or phen-ethyl), which are bound directly or with a binder molecule to the polyester or polycarbonate. The binder molecule is preferably chosen from

$-O-$, $-S-$, $-NH^4-$, .. *Chemical formulas - see original - Line 25*

(the propargyl group is bonded to X)

whereby R^4 stands for H, C_1 - C_4 -alkyl or phenyl, X for O, S, or NR^2 , and R^2 for H, C_1 - C_4 -alkyl or phenyl.

The propargyl group is preferably bonded to the polyester through

Chemical formulas - see original - Line 35

The polyester contain preferably

(IX) at least an aromatic or aliphatic di-carbonic acid unit and/or at least an aromatic or aliphatic hydroxy-carbonic acid unit, and

(X) at least one diol unit.

Preferred di-carbonic acid units are those of following formula:

- 11 -

Chemical formulas - see original - Line 1

especially those of the formula

Chemical formulas - see original - Line 35

or

Chemical formulas - see original - Line 45

whereby each phenyl group or naphthalene group can feature 1, 2, or 3 substituents, which can be chosen independent of each other from C₁-C₄-alkyl, C₁-C₄-alkoxy, halogen or phenyl, whereby "W" stands in the above formula for NR, S, O, (CH₂)_pO(CH₂)_q, (CH₂)_m, or a single bond,

R for alkyl or hydrogen,

m for a whole number from 1 to 15, and

"p" and "q" independent from each other for whole numbers from 0 to 10.

Preferred hydroxy-carbonic acid units are those with following formula:

Chemical formulas - see original - Line 55

whereby each phenyl group or naphthalene group can feature 1, 2, or 3 substituents, which can be chosen independent of each other from C₁-C₄-alkyl, C₁-C₄-alkoxy, halogen or phenyl.

Preferred diol units are those with following formula:

- 12 -

Chemical formulas - see original - Line 1

especially those with the formula:

- 13 -

Chemical formulas - see original - Line 1

whereby the meaning in the above formulas for

L is alkyl, alkoxy, halogen, COOR, OCOR, CONHR, or NHCOR,

X is S, O, N, CH₂, or a single bond,

A is a single bond, (CH₂)_n, O(CH₂)_n, S(CH₂)_n, NR(CH₂)_n,

Chemical formulas - see original - Line 30

R stands for alkyl, or hydrogen, and

R¹ hydrogen, halogen, alkyl, or phenyl, and

n for a whole number from 1 to 15.

Preferred are polyester, which contain at least a di-carbonic acid of the formula

Chemical formulas - see original - Line 45

and at least a diol unit of the formula

Chemical formulas - see original - Line 60

whereby R³ stands for H, halogen, C₁-C₄-alkyl especially CH₃ or C(CH₃)₃, or phenyl.

Other preferred components are di-esters of the formula P-Y-B-CO-O-A-O-CO-B-Y-P, whereby P stands for propargyl-terminal groups according to the above defined formula, Y for O, S, or NR₂(R²=C₁-C₄-alkyl), B for

- 14 -

Chemical formulas - see original - Line 1

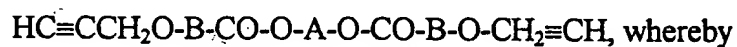
whereby each phenyl group or the naphthalene group can feature 1, 2, or 3 substituents, which can be selected independently of each other from C₁-C₄-alkyl, C₁-C₄-alkoxy, halogen or phenyl, and A (together with neighboring oxygen atoms) for one of the above named diol

units.

Especially preferred di-ester are those of the above stated formula, whereby B stands for

Chemical formulas - see original - Line 10

and especially for di-ester of the formula



(XI) B for

(XII)

Chemical formulas - see original - Line 20

and A stands for

Chemical formulas - see original - Line 25

or

(XII) B for

Chemical formulas - see original - Line 40

and

A having the meaning given under XI.

Additional preferred components are polycarbonates, which contain at least a diol unit of the above given formula, especially of the formula

Chemical formulas - see original - Line 55

or

Chemical formulas - see original - Line 60

Preferred polycarbonates are in this case those, which contain as diol units at least a mesogenic unit of the formula

Chemical formulas - see original - Line 1 and

at least a chiral unit of the formula

Chemical formulas - see original - Line 10

and possibly a non-chiral unit of the formula

Chemical formulas - see original - Line 15

whereby R^1 has the above stated meaning and especially stands for H or CH_3 .

Especially preferred polycarbonates are those with propargyl-terminal groups of the formula $HC\equiv CCH_2O-R^5-CO$, whereby R^5 stands for

Chemical formulas - see original - Line 25

Moreover, suitable as polymers of group c) are cholesteric polycarbonates which also contain photoreactive groups in a non-terminal position. These polycarbonates are described in DE-A-196 31 658. They correspond preferably to Formula XIII

Chemical formulas - see original - Line 35
(XIII)

whereby the molar ratio $w/x/y/z$ is about 1 to 20 / about 1 to 5 / about 0 to 10 / about 0 to 10. Most preferred is a molar ratio $w/x/y/z$ is about 1 to 5 / about 1 to 2 / about 0 to 5 / about 0 to 5.

In formula XIII

A stands for a mesogenic group with the formula

Chemical formulas - see original - Line 50

B for a chiral group of the formula

- 16 -

Chemical formulas - see original - Line 1

D stands for a photoreactive group with the formula

Chemical formulas - see original - Line 50

or

Chemical formulas - see original - Line 55

and

E for another, non-chiral group of the formula

- 17 -

Chemical formulas - see original - Line 5

whereby the symbols in the above formulas stand for the following:

L for alkyl, alkoxy, halogen, COOR, OCOR, CONHR, or NHCOR,

X is S, O, N, CH₂, or a single bond,

R for alkyl or hydrogen,

A for a single bond, (CH₂)_n, O(CH₂)_n, S(CH₂)_n, NR(CH₂)_n,

Chemical formulas - see original - Line 15

or

Chemical formulas - see original - Line 20

R¹ stands for hydrogen, halogen, alkyl, or phenyl, and

n for a whole number from 1 to 15.

If R¹ stands for an alkyl, halogen, and A for a single bond, or if R¹ stands for H or alkyl, and A for

Chemical formulas - see original - Line 30

is a solubility improved group. Examples of this are

Chemical formulas - see original - Line 35

Isosorbide, isomannide, and/or isoidide are preferred chiral components.

The amount of chiral diol-structure units is preferably in the range of 1 to 80 mol-% of the total content of diol structure units depending on the desired reflection behavior.

Preferred polymers of group d) are, for example, crosslinkable, cholesteric copoly-isocyanates such as those described in US-A-08 834 745, which are hereby incorporated in their entirety. These copoly-isocyanates feature repeating units in the formula

Chemical formulas - see original - Line 50

and possibly with the formula

- 18 -

Chemical formulas (V) - see original - Line 5

whereby

R¹ stands for a chiral aliphatic or aromatic rest,

R² stands for a crosslinkable rest, and

R³ stands for an achiral rest.

Insofar as nothing else is stated, the term "alkyl" (also in the meaning of alkoxy, dialkyl, alkylthio, etc.) is understood to be a branched or a straight C₁-C₁₂-alkyl, preferably C₁-C₁₂, and most preferably C₁-C₁₀, especially a C₆-C₁₀-alkyl.

Preferably R¹ is chosen from (chiral) branched or straight alkyl, alkoxy-alkyl, alkylthio-alkyl, cyclo-alkyl, alkyl-pentenyl, or C₃-C₉-epoxy-alkyl rests, or rests of esters of C₁-C₆-fatty acids with C₁-C₆-alkanols or C₃-C₉-dialkyl-ketones. The ester rests can be bound to the N-atom either through the fatty acid portion, or as well through the alcohol rest. The rest R¹ can carry 1, 2, or 3 substituents which can be the same or different, and can be chosen from the alkoxy groups, di-C₁-C₄-alkyl-amino groups, CN, halogen atoms, or C₁-C₄-alkylthio groups.

Preferably R^1 is chosen from alkyl, alkoxy-alkyl, rests of esters of C_1 - C_6 -fatty acids with C_1 - C_6 -alkanols or C_3 - C_9 -dialkyl-ketones and epoxy functional C_3 - C_9 -epoxy-alkyl rests, whereby R^1 can have been substituted with 1 or 2 rests, which can be of the same or a different kind, and be chosen from alkoxy, halogen, CN, or CF_3 . Preferred substituents for branched and straight chain alkyl and alkoxy rests are chosen from alkoxy groups, halogen atoms, or CN; for esters of C_1 - C_6 -fatty acids with C_1 - C_6 -alkanols from alkoxy-groups, halogen atoms, CN, or CF_3 , and for C_3 - C_9 -di-alkyl-ketones from alkoxy groups, halogen atoms, or CN.

In particular, the main chain of rest R^1 features a length of 3 to 12, especially 6 to 10, and preferably 6 to 8 parts (C-, O-, and/or S-atoms). Most preferred are rests of R^1 , which have been chosen from

Chemical formulas - see original - Line 30

- 19 -

Chemical formulas - see original - Line 5 - 60

- 20 -

Chemical formulas - see original - Line 5

Particularly preferred as component III is use of the copoly-isocyanates derived from 2,6-dimethylheptyl-isocyanate.

The rest R^2 of the used copoly-isocyanates is preferably chosen from C_3 - C_{11} -alkenyl rests, C_4 - C_{11} -vinylether rests (=vinyl- C_2 - C_9 -alkyl ethers), ethylenically unsaturated C_3 - C_{11} -carbonic acid esters, and esters of ethylenically unsaturated C_3 - C_6 -monocarboxylic acids with C_2 - C_6 -alcohols, whereby the bond to the N-atom occurs through the alkanol rest of the ester. The rest is chosen especially preferred from methylacrylate, ethylacrylate, propylacrylate, n-butyl-acrylate, isobutyl-acrylate, 2-ethyl-hexyl-acrylate, methylmethacrylate, ethylmethacrylate, propylmethacrylate, n-butyl-methacrylate, isobutyl-methacrylate, 2-ethylhexyl-methacrylate, especially from ethylacrylate or ethylmethacrylate.

Rest R^3 preferably has the same meaning as rest R^1 . However, it is achiral, i.e. it does not exhibit a chirality center or is present as a "racemic" (?) mixture.

Especially preferred is a main chain of rest R^3 with a length of 4 to 12, especially 6 to 10, and most preferred 6 to 8 parts (C-, O-, and/or S-atoms). Most preferred is the component V of the copoly-isocyanate of this invention derived from n-hexyl-isocyanate, n-heptyl-isocyanate, or n-octyl-isocyanate.

Components III, IV, and V are preferably present in mol amounts of III : IV : V of about 1 to 20 : 1 to 20 : 50 to 98, especially 5 to 15 : 5 to 15 : 65 to 90, and most preferably 15 : 10 : 75.

The units II, IV, and V can be statistically distributed in the copoly-isocyanate where they are utilized.

Suitable polymers of group e) are chiral nematic polyester with flexible chains, which comprise isosorbide, isomannide, and/or isoidide units, preferably isosorbide units, and contain at least one unit to render the chain more flexible, which are chosen (and derived) from

- a) aliphatic dicarbonic acids
- b) aromatic dicarbonic acids with flexible spacer
- c) α,ω -alkanoids
- d) diphenols with flexible spacer, and
- e) condensation product of a polyalkylen-terephthalate or polyalkylen-naphthalene with an alkylated diphenol and an alkylated isosorbide

as described in DE-A-197 04 506.

The polyester are not crystalline and form a stable, cholesteric phase, which can be frozen during cooling below the glass transition temperature. The glass transition temperature of the polyester is again despite the flexibility above 80 °C, preferably above 90 °C, and especially above 100 °C.

The usable polyester contain as unit a) preferably those of formula



whereby "n" is a number in the range from 3 to 15, especially 4 to 12, and most preferably adipic acid; it contains as unit b) preferably those of formula

Chemical formula - see original - Line 55

whereby

A is $(\text{CH}_2)_n$, $\text{O}(\text{CH}_2)_n\text{O}$, or $(\text{CH}_2)_o-\text{O}-(\text{CH}_2)_n$,

"n" a number in the range of 3 to 15, especially 4 to 12, and most preferred 4 to 10, and

"o" and "p" independent of each other a number in the range of 1 to 7;

it contains as unit c) preferably those of formula



whereby

"n" is a number in the range of 3 to 15, especially 4 to 12, and most preferred 4 to 10, and
 "m" a number in the range of 1 to 10; and

it contains as unit c) preferably those of formula

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Chemical formula - see original - Line 1

whereby

A is $(CH_2)_n$, $O(CH_2)_nO$, or $(CH_2)_o-O-(CH_2)_n$,

"n" a number in the range of 3 to 15, especially 4 to 12, and most preferred 4 to 10, and
 "o" and "p" independent of each other a number in the range of 1 to 7.

The usable polyester contain moreover as a non-flexible acid component, preferably dicarbonic acid units of the formula

Chemical formulas - see original - Line 15

and as non-flexible alcohol components diol units of the formula

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Chemical formulas - see original - Line 1

whereby in the above formulas

L stands for alkyl, alkoxy, halogen, COOR, OCOR, CONHR, or NHCOR,

X for S, O, N, CH_2 , or a single bond, and

A stands for a single bond of

Chemical formulas - see original - Line 50

whereby

R^1 stands for hydrogen, halogen, alkyl, phenyl, and
R for alkyl or hydrogen.

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The usable polyesters may possibly contain additional flexible diol units of the formula

Chemical formulas - see original - Line 1

whereby

R^1 stands for hydrogen, halogen, alkyl, phenyl, and
A $(CH_2)_n$, $O(CH_2)_nO$, $S(CH_2)_n$, or $NR(CH_2)_n$, and
"n" a number from 1 to 15.

Preferred polymers of group f) are, for example, crosslinkable, liquid-crystal polyorganosiloxanes, as are described in BP-A-066 137 and in EP-A-358-208. Furthermore, the mixture of group f) contains a chiral component. Suitable chiral components are especially those chiral doping materials of Formula 1a described for the mixture of group b).

The heat insulation coating of this invention contains most preferred chiral components and nematic monomers according to group b), especially chiral components of Formula 2:

Chemical formulas - see original - Line 30 (2)

and/or Formula 5

Chemical formulas - see original - Line 35 (5)

and nematic monomers of Formula 1:

Chemical formulas - see original - Line 45 (1)

of Formula 3:

Chemical formulas - see original - Line 55 (3)

or of Formula 4:

Chemical formulas - see original - Line 65 (4)

in cured condition, whereby n_1 and n_2 are independent of each other in Formulas 1 and 3 standing for 2, 4, or 6, and the monomers of Formula 1 or 3 are preferably used in mixtures of the components with ratios of $n_1/n_2 = 2/4, 2/6, 4/2, 6/2, 4/4, 4/6, 6/4, \text{ or } 6/6$, and R standing in Formula 4 for H, Cl, or CH_3 .

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Another subject of the present invention is a process to produce a heat insulation coating, which is characterized by applying on a transparent substrate at least one cholesteric, IR-reflecting layer, curing it, adding possible one or several additional cholesteric IR-reflecting layers, as well as possibly a medium reversing the sense of rotation of the transmitted circular-polarized light, curing it, and thereby completing the heat insulation coating.

The transparent substrate to which the IR-reflecting layer(s) is/are applied, can be a brick of glass, for example, or a window pane, or a film which is to be glued to the window pane for insulation purposes.

The application of the cholesteric, IR-reflecting layer on the substrate can occur by typical processes, for example, by a process which is chosen from air-blade coating, blade coating, air-knife coating, roll coating, immersion coating, reverse-roll coating, transfer roll coating, gravure coating, "kiss-coating", slide coating, spray coating, spin coating, or printing processes such as high print, low print, flexo-print, offset, or screen printing.

The IR-reflecting layer(s) can be applied to the substrate at low or high viscous, preferably however at low viscosity. The cholesteric mixtures are applied undiluted or diluted for this purpose to the substrate at elevated temperature or diluted at low temperature.

The formulations containing cholesteric mixtures or adsorption pigments can be diluted with any suitable diluent before applying them to the substrate.

Diluents used as examples in the process of this invention for components a) or b) are linear or branched esters, especially acetic acid ester, cyclic ethers and esters, alcohols, lactones, aliphatic and aromatic hydrocarbons such as toluene, xylene, and cyclohexane, as well as ketones, amides, n-alkyl-pyrrolidone, especially N-methyl-pyrrolidone, and especially tetrahydrofuran (THF), dioxane, and methylethylketone (MEK).

Suitable diluents for the polymers of group c) are, for example, ether and cyclic ethers such as tetrahydrofuran or dioxane, chlorinated hydrocarbons such as dichloromethane, 1,1,2,2-

tetrachlorethane, 1-chloro-naphthalene, chlorobenzene, and 1,2-dichlorobenzene. These diluents are especially suitable for polyesters and polycarbonates. Suitable diluents for cellulose derivatives are, for example, ethers such as dioxane, or ketones such as acetone. If copoly-isocyanates are used as polymers of group d), it makes sense to utilize polymerizable diluents as described in US-A-08 834 745. These polymerizable diluents are, for example,

- ester of α,β -unsaturated mono or dicarbonic acids, especially C_3 - C_6 -mono or dicarbonic acids, with C_1 - C_{12} -alcohols, C_2 - C_{12} -alkane-diols, or their C_1 - C_6 -alkyl-ether and phenyl-ether, for example acrylate and methacrylate, hydroxy-ethyl or hydroxy-propyl-acrylate, or methacrylate such as 2-ethoxy-ethyl-acrylate or methacrylate;
- vinyl- C_1 - C_{12} -alkyl-ether such as vinyl-ethyl, vinyl-hexyl, or vinyl-octyl-ether;
- vinyl-ester of C_1 - C_{12} -carbonic acids such as vinylacetate, vinyl-propionate, vinyl-laureate;
- C_3 - C_3 -epoxies such as 1,2-butylene-oxide, styrol-oxide;
- N-vinyl-pyrrolidone, N-vinyl-caprolactame, N-vinyl-formamid
- vinyl-aromatic components such as styrene, α -methyl-styrene, chloro-styrene, and
- components with two or more crosslinkable groups such as diesters of diols (including polyethylene glycol) with acrylic or methacrylic acid or divinyl-benzol.

Examples of preferred polymerizable diluents are 2-ethoxy-ethyl-acrylate, diethylene-glycol-diacrylate, ethylene-glycol-dimethacrylate, diethylene-glycol-dimethacrylate, triethylene-glycol-dimethacrylate, diethylene-glycol-monomethyl-ether-acrylate, phenoxy-ethyl-acrylate, and tetra-ethylene-glycol-dimethacrylate. A particular preferred polymerizable diluent is styrene.

The mixtures of groups a), b), or c) can also contain in small amounts polymerizable diluents. Preferred polymerizable diluents which can be added to a), b), or c) are acrylates, particularly high-functional acrylates such as bis, tris, or tetra-acrylates, especially preferred are high boiling oligo-acrylates. The preferred amount of additive is at about 5 %w relative to the total amount of weight.

The cholesteric mixture can contain commercially available photoinitiators for photochemical polymerization. They are not necessary for curing with electron beam radiation. Suitable photoinitiators are, for example, isobutyl-benzoinether, 2,4,6-trimethyl-benzoyl-diphenyl-phosphine oxide, 1-hydroxy-cyclo-hexyl-phenyl ketone, 2-benzyl-2-dimethyl-amino-1-(4-morpholino-phenyl)-furan-1-on, mixtures of benzophenone and 1-hydroxy-cyclo-hexyl-phenyl ketone, 2,2-dimethoxy-2-phenyl-acetophenon, perfluorinated diphenyl-titanium-ocene, 2-methyl-1-(4-[methyl-thio]phenyl)-2-(4-morpholinyl)-1-propanon, 2-hydroxy-2-methyl-1-phenyl-propane-1-on, 4-(2-hydroxy-ethoxy)phenyl-2-hydroxy-2-propyl ketone, 2,2-diethoxy-acetophenone, 4-benzoyl-4'-methyl-diphenyl-sulfide, ethyl-4-(dimethyl-amino)benzoate, mixtures of 2-isopropyl-thioxanthone and 4-isopropyl-thioxanthone, 2-(dimethyl-amino)ethyl-benzoate, d,l-champher-chinon, ethyl-d,l-champher-chinon, mixtures of benzophenone and 4-methyl-benzophenone, benzophenone,

4,4-bisdimethylamine-benzophenone, (η^5 -cyclopentadienyl) (η^6 -isopropylphenyl)-iron(II)-hexafluoro-phosphate, triphenyl-sulfonium-hexafluoro-phosphate, or mixtures of triphenyl-sulfonium salts, as well as butane-diol-diacrylate, dipropylene-glycol-diacrylate, hexane-diol-diacrylate, 4-(1,1-dimethyl-ethyl)-cyclo-hexyl-acrylate, trimethylol-propane-triacrylate, and tripropylene-glycol-diacrylate.

The cholesteric mixture can be mixed with additional compounds to adjust the viscosity and the processing behavior.

For example, polymer binders and/or monomeric binders, which are transformed by the polymerization into polymeric binders can be utilized. Suitable as these kind of materials are, for example, polyester, cellulose ester, polyurethanes, silicones, polyether- or polyester-modified silicones which are soluble in organic solvents.

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Even the addition of small amounts can favorably influence the processing. As example, about 0.005 to 1 %w, especially 0.01 to 0.5 %w relative to the amount of cholesteric material can be utilized. Suitable processing aides are, for example, glycols, silicone oils, and especially acrylate polymers such as those acrylate-copolymers commercially available under the trade name Byk 361 or Byk 358 from Byk-Chemie Co., and the modified, silicone-free acrylate polymers available from Tego Co. under the name Tego flow ZFS 460.

The cholesteric mixtures can possibly also contain stabilizers against UV-light and weathering influences. Suitable for this purpose are, for example, derivatives of 2,4-dihydroxy-benzophenone, derivatives of 2-cyan-3,3-diphenyl-acrylates, derivatives of 2,2',4,4'-tetra-hydroxy-benzophenone, derivatives of ortho-hydroxy-phenyl-benzotriazol, salicylic acid esters, ortho-hydroxy-phenyl-S-triazine, or sterically hindered amines. These materials can be utilized alone or preferably in form of mixtures.

The applied IR-reflecting layer(s) can be cured thermally, photochemically, or by electron beam radiation.

The curing on the cholesteric phase has to obviously occur while maintaining the cholesteric phase.

If several layers are applied, they can each be applied individually, possibly dried and cured. However, it is also possible to apply several or all layers, which are to be applied, in one application step wet-on-wet on the substrate to be coated, possibly drying them together and curing them together. A prerequisite for the simultaneous application of the cholesteric layers is, however, that interdiffusion does not take place between the various layers with different reflection characteristics.

Slide coating methods are especially well suited for the simultaneous application of the cholesteric layers, especially with knife, or blade coating, extrusion or scrape, and the cascade-slide coating. The listed slide coating methods are described, for example, in DE-A-19 504 930, in EP-A-431 630, in DE-A-3 733 031, as well as in EP-A-452 959, which are hereby explicitly referenced.

Another subject of the present invention is a multi-component-coating system comprising components, which are capable of creating cholesteric layers with reflection maxima different from each other in the wavelength range > 750 nm. A substrate can be equipped with a heat-insulating coating of this invention with the help of these kind of coating systems of this invention, whose components can be utilized in resin formulations, for example.

The heat-insulating coating of this invention can especially be used for production of insulation windows, or heat-insulated transparent building materials, or for insulation of residential, office, or industrial buildings against radiant heat. Furthermore, the heat-insulating coating of this invention is also particularly suitable for use in the field of automobiles, especially for the production of heat-insulating composite window panes. Their use for this purpose is therefore another subject of the present invention.

The following Examples 1 to 3 explain the invention without limiting the invention to the examples.

A nematic, liquid-crystalline mixture of Formula I was used for Examples 1 to 3, which is present up to 5°C in the smectic, up to 68°C in the nematic, and above 68°C in the isotropic phase (S5 N 68 I).

The component of Formula 2 was added as chiral doping material in Examples 1 and 2, and in Example 3 the component of Formula 5.

To improve the film formation of the utilized mixtures in Examples 1 to 3, cellulose-acetate-butyrates was added at a concentration of 0.8 %w relative to the cholesteric mixture, and the whole mixture was dissolved in butyl-acetate.

2,4,6-trimethyl-benzoyl-diphenyl-phosphine-oxide was added as photoinitiator at a concentration of 1.5 %w relative to the cholesteric mixture. This mixture was applied with a knife to a glass plate at a wet thickness of $30\text{ }\mu\text{m}$. A homogeneous, transparent layer was obtained in all three examples after the solvent had evaporated. The layer was photochemically crosslinked with a UV-light source.

Example 1

Five cholesteric layers were each applied individually and cured as described above. The composition of the cholesteric layers differ in the concentration of their content material which can be taken from the following Table 1:

Layer	x_{ch}	x_n	λ_R
1	0.032	0.968	220
2	0.027	0.973	943
3	0.024	0.974	1085
4	0.021	0.979	1250
5	0.018	0.982	1440

All layers contained additionally cellulose-aceto-butyrate and 2,4,6-trimethyl-benzoyl-diphenyl-phosphen-oxide at the above stated concentrations. The concentration of the chiral component is abbreviated with x_{ch} and given as molar ratio.

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The concentration of the nematic component is abbreviated with x_n and also given as a molar ratio. λ_r states the wavelength of the reflection maximum in nm.

The applied, superimposed layers exhibit a reflection of 47% of the incident amount of light in the wavelength between 752 and 1500 nm. The transparency in the visible wavelength region (between 400 and 700 nm) was over 90%.

Example 2

The mixture contained in layer 1 in Example 1 was used for Example 2. This mixture was as stated above applied with a knife at a wet film thickness of 30 μm to two glass plates, the solvent was removed, and the resulting transparent film was cured photochemically by means of a UV-light source (Nitraphot-lamp, OSRAM CO.). Afterwards, a $\lambda/2$ -film (Nitto Co.) was placed such between the two coated glass plates, that the liquid-crystalline layers were in contact with the $\lambda/2$ film. The optical properties of this arrangement were studied by spectroscopy. It was found that the coating containing the $\lambda/2$ film had a degree of reflection in the wavelength range from 752 to 880 nm of 89% and a transmission in the visible wavelength range of over 93%.

Example 3

Two layers were each applied one at a time on top of the other by means of a knife with a wet film thickness of 30 μm , the solvent was removed, and the resulting film of about 16 μm , which is transparent in the visible range, was photochemically cured with the above listed light source. The two layers located on top of each other were chemically identical in regard to their material composition; they each contained 13 molar parts cholesteric material per 87 molar parts of nematic component such as cellulose-aceto-butyrate and 2,4,6-trimethyl-benzoyl-diphenyl-phosphene-oxide at the above given amounts. The wavelength of the reflection maximum was for both layers at 820 nm. However, the layers were different in their chirality; the helical superstructure of the one layer was right oriented, that of the other layer was left-oriented. Spectroscopic studies showed a selective reflection of 94% at a wavelength of 820 nm. The half-width value of the reflection was 121 nm. The transmission in the visible wavelength region was over 93%.

Patent Claims

1. Heat-insulating coating comprising one or several cholesteric layers, which reflect at least 40%, especially at least 45% of the incident radiation in the infrared wavelength region, preferably above 750 nm, especially in the wavelength region from 751 to about 2000 nm,.
2. Heat-insulating coating according to Claim 1, which features a transmission of at least 80%, especially at least 90% of the incident radiation in the wavelength region of about 390 nm to 750 nm.
3. Heat-insulating coating according to one of the previous claims, which comprises several, preferably 2 to 20, especially about 2 to 10 cholesteric IR-reflecting layers.
4. Heat-insulating coating according to Claim 3, whose cholesteric layers feature reflection maxima in the wavelength range >750 nm, which are different from each other.
5. Heat-insulating coating according to one of the previous claims, which comprises several cholesteric layers, preferably a number of cholesteric layers which can be divided by 2, whereby the stepping height of the helical superstructure of each of two layers is the same, but their chirality different.
6. Heat-insulating coating according to one of the previous claims, which features a medium between layers of a helical superstructure with the same stepping height and the same chirality, whose sense of orientation of the transmitted, circular-polarized light is reversed, especially a so-called $\lambda/2$ film or plate.

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7. Heat-insulating coating according to Claim 6, which reflects the incident light by at least 75%, especially at least 85% in the wavelength region above 750 nm, especially in the wavelength region from 751 nm to about 200 nm.
 8. Heat-insulating coating according to one of the previous claims, which contains in cured condition cholesteric components or mixtures of components, which have been chosen from
 - a) at least one cholesteric polymerizable monomer;
 - b) at least one achiral, nematic polymerizable monomer and a chiral component;
 - c) at least one cholesteric, crosslinkable polymer
 - d) at least one cholesteric polymer in a diluent or a mixture of diluent which can be polymerized;
 - e) at least one cholesteric polymer, whose cholesteric phase can be frozen by rapid cooling below the glass transition temperature; or
 - f) at least one achiral, liquid-crystalline crosslinkable polymer and a chiral component.
 9. Process for producing a heat-insulating coating according to one of the previous claims, characterized by applying at least one cholesteric, IR-reflecting layer to a transparent substrate, curing it, possibly applying one or several more cholesteric, IR-reflecting layers, as well as possibly a medium which reverses the sense of rotation of transmitted, circular-polarized light, curing it and thereby completing the heat-insulating coating.
 10. Multiple-component coating system, comprising components which are capable of forming cholesteric layers according to the definition in one of the Claims 4 to 8.
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11. Application of the heat-insulating coatings according to one of the Claims 1 to 8 for the production of insulating windows or heat-insulating, transparent building materials, or as insulators for domestic, office, or industrial buildings.
 12. Application of the heat-insulating coatings according to one of the Claims 1 to 8 in the automobile area, especially for producing heat insulated composite window panes.
 13. Film, especially an adhesive film, comprising a heat-insulating coating according to one of the Claims 1 to 8.